Short communication

Enhanced selectivity for the electrochemical reduction of CO_2 to alcohols in aqueous solution with nanostructured Cu–Au alloy as catalyst

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HIGHLIGHTS

- Nanostructured Cu–Au alloy was tested as electro-catalyst for CO_2 reduction.
- Au component contributed greatly to the conversion of CO_2 to alcohols.
- Faradic efficiency of CH_3OH on nano $Cu_{63.9}Au_{36.1}$ was 19 times that on Cu plate.

GRAPHICAL ABSTRACT
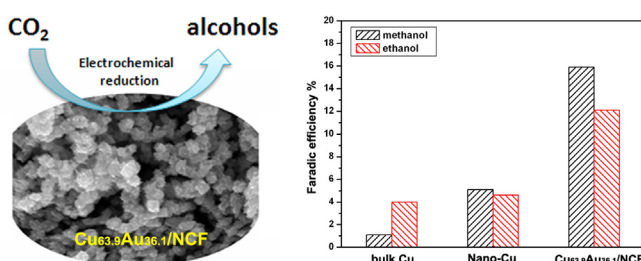
ABSTRACT

Electrochemical reduction of CO_2 in an aqueous 0.5 M $KHCO_3$ solution is studied by use of novel nanostructured Cu–Au alloys, which are prepared through electrochemical deposition with a nano-porous Cu film (NCF) as template. Linear voltammetry results show that the as-synthesized Cu–Au alloys exhibit obvious catalysis towards electrochemical reduction of CO_2. Further analysis of products reveals that faradic efficiencies of alcohols (methanol and ethanol) are greatly dependent on the nanostructures and compositions of Cu–Au alloys. It is expected that this work could provide new insight into the development of powerful electrocatalysts for reduction of CO_2 to alcohols.

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1. Introduction

Direct electrochemical reduction of CO_2 has attracted much attention over recent decades as this offers a convenient route to convert waste CO_2 into useful organics [1,2]. In addition, this process provides a potential solution for the storage of energy in chemical fuels for energy sources. For example, electricity from renewable solar power could be stored in chemical form via electrochemical reduction of CO_2 [3]. And the reduction products can be sources for automobile fuels or generation of electricity again by fuel cells. Amongst various possible products of CO_2 reduction in aqueous system, alcohols such as methanol and ethanol are desirable owing to their high energy density and easy transportation. However, the conversion efficiencies of CO_2 to alcohols on metal-based catalysts are still very low by present. To improve the conversion efficiency of CO_2 to alcohols, it is essential to develop new electrocatalysts.

Hori et al. have demonstrated that the product selectivity during CO_2 reduction is in fact very sensitive to the electro-catalysts used [1]. Among pure metallic electrodes, only copper electrode is demonstrated to be able to catalyze the conversion of CO_2 to alcohols [4]. Unfortunately, faradic efficiencies of alcohols are

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relatively low (less than 1% for methanol) and major products are CO, formate and hydrocarbons [5]. A recent report showed that Cu_2O electrode could catalyze the conversion of CO_2 to methanol with a high faradaic efficiency of 38% [6]. However, the Cu_2O tended to be reduced and lost catalytic function. In comparison, considerable progress has been achieved on the conversion of CO_2 to CO with faradic efficiency up to 96% [7]. The reason could be that CO is initially produced before the formation of alcohols at more negative potentials. Although the formation mechanism of alcohols is not clear in detail, it is widely accepted that CO_2 is initially reduced to CO, which is further converted to alcohols or other hydrocarbons. Considering that the reduction of CO_2 to alcohols goes through multistep electron-transfer pathways, sole Cu metal may not be

capable of catalyzing the conversion of CO_2 to alcohols efficiently. Therefore, Cu alloys were tried in the electrochemical reduction of CO_2 and showed distinct behaviors from those of pure metals [8]. These results indicated that development of new electrocatalysts based on the composites of Cu and other metals could be a possible way to improve the yield of alcohols.

In this article, nanostructured Cu–Au alloys were synthesized for electrochemical reduction of CO_2 in aqueous solution for the first time. To ensure clean surface of catalysts, no organic additives were used and nanostructured Cu–Au alloys were obtained by electrochemical deposition with a nanoporous Cu film (NCF) as template. It has been proven that gold material (no matter in bulk size or nanoscale size) only catalyzed conversion of CO_2 to CO, not
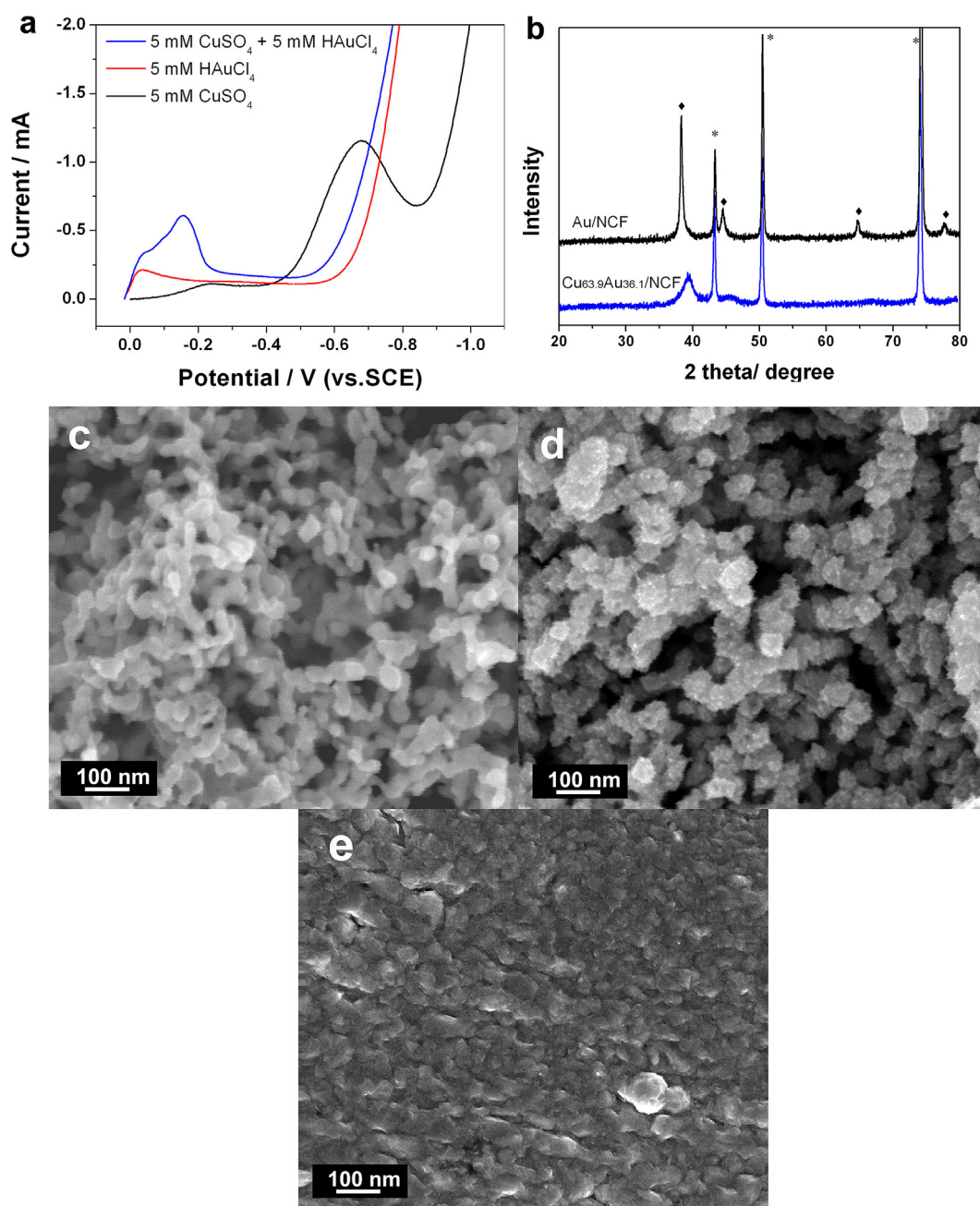
Fig. 1. (a) LSV curves of polished Cu working electrode (7 mm^2 exposed area) in 0.1 M H_2SO_4 containing $CuSO_4$, $HAuCl_4$, and $CuSO_4$ + $HAuCl_4$, respectively. (b) XRD patterns of deposits on NCF electrode prepared by electro-deposition. The mark of ◆ and * represents the peaks from pure Au (JCPDS file card No. 2-1095) and Cu (JCPDS file No. 89-2838), respectively. (c, d) SEM images of NCF (c) and Cu–Au sample deposited on NCF (d). (e) SEM image of the Cu–Au deposited on smooth Cu at potential of −0.26 V.
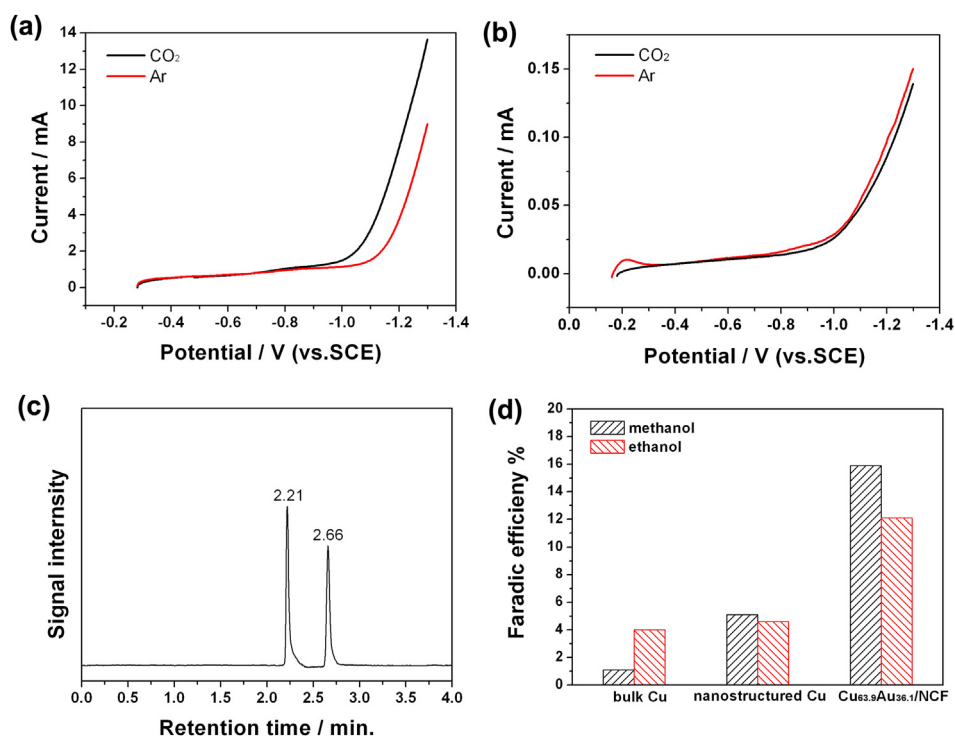
Fig. 2. LSV curves of $Cu_{63.9}Au_{36.1}$/NCF (a) and Cu nanoparticles (b) in 0.2 M PBS solution saturated with CO_2 (black line) and Ar (red line). (c) GC spectrum of liquid products of CO_2 reduction on $Cu_{63.9}Au_{36.1}$/NCF electrode. (d) Faradic efficiencies of methanol and ethanol by use of different electrodes in 0.5 M $KHCO_3$ solution (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

alcohols [9]. But here addition of gold into copper alloy brought surprising catalytic activity towards conversion of CO_2 to alcohols. While it is possible to vary film morphology and structure, in this communication we examine only the effect of varying the alloy composition on conversion efficiency of CO_2 to alcohols, demonstrating encouraging results for these novel catalysts.

2. Experimental

2.1. Fabrication of nanostructured Cu−Au alloys for electro-catalytic reduction of CO_2

NCF/Cu electrode was prepared by a similar process published in our previous work [10]. In brief, NCF/Cu electrode was fabricated by electrochemical dealloying of thermal-treated Cu−Zn sample in 25 mM HCl using linear sweep voltammetry (LSV). With the NCF/Cu electrode as working electrode (2 cm^2 exposed area), electrodeposition of nanostructured Cu−Au alloy was conducted under constant potential in solution containing 0.1 M H_2SO_4, 5 mM $CuSO_4$, and 5 mM $HAuCl_4$. A saturated calomel electrode (SCE) and a platinum plate were used as reference electrode and counter electrode, respectively. The total deposition charge was set to 0.2 C. The as-synthesized Cu−Au alloy electrodes were then used as working electrode and immersed into electrolyte with 2 cm^2 exposed area. The electrochemical behaviors of Cu−Au alloy electrodes were evaluated by LSV in a phosphate buffered solution (PBS, 0.2 M Na_2SO_4, 0.2 M NaH_2PO_4−Na_2HPO_4, pH 7.6) saturated with either CO_2 or Ar. Bulk electro-reduction of CO_2 was performed in an H-type cell separated by a cation exchange membrane (Nafion 117). Before this electrolysis, a catholyte of 0.5 M $KHCO_3$ solution was bubbled with Ar to remove oxygen and then saturated with ultrapure CO_2 (99.999%) by bubbling for 30 min (298 K, pH 7.6). Bulk electrolysis was carried out at −1.1 V (vs. SCE) and total

consumed charge was 8 C per sample. For the test of Cu or Au nanoparticles, 8 mg powder of Cu nanoparticles (20−40 nm, Alfa Aesar) or Au nanoparticles (20−25 nm, Alfa Aesar) were ultrasonically dispersed in 1 mL Nafion solution (0.5 wt%) and 0.25 mL of mixture was dropped onto a carbon cloth (2 cm^2 area, Japan, NOK-H2315 GDL) as nanostructured electrode. These were then dried in a vacuum-oven at 50 °C for 2 h to remove residual alcohols of Nafion solution.

2.2. Characterization and analysis of products

The morphologies of samples were observed using a JEOL-6700F field emission scanning electron microscopy (FESEM). X-ray diffraction (XRD) patterns were recorded on a Philips MPD 18801 diffraction-meter (CuKα radiation, $\lambda = 1.5418$ Å, 20 kV, 150 mA). The surface compositions of Cu−Au deposits were analyzed through X-ray photoelectron spectroscopy (XPS) on a spectrometer (VG Scientific ESCALAB Mark II, Al anode). The concentrations of methanol and ethanol produced in solution by the electrochemical reduction of CO_2 were analyzed using a gas chromatograph (GC, Hengxin GC-2020) equipped with FID detector and capillary column (PEG-20M). To avoid damage to the GC caused by the presence of salt in the

Table 1
Faradic efficiencies of main liquid products with different electrodes.

Electrode	Faradic efficiencies %	
	Formate	Alcohols (methanol and ethanol)
Bulk Cu	11.5	4.8
Nanostructured Cu	27.4	9.7
$Cu_{63.9}Au_{36.1}$/NCF	12.6	28
$Cu_{70.6}Au_{29.4}$/NCF	18.1	17.2
$Cu_{81.3}Au_{19.7}$/NCF	21.2	11.5

solutions, the electrolyte was mixed with Amberlite IRN-150 ion-exchange resin (Alfa Aesar) and filtered to remove $KHCO_3$ before GC analysis [11]. The temperatures of injector and detector were both held at 200 °C. After injection of 1 μL solution sample, the oven temperature was held at 40 °C for the first 4 min, which was optimum for the separation of methanol and ethanol components. Then the oven temperature was increased to 120 °C at 20 °C min^{-1} to remove the water from GC completely. The concentration of formate in liquid products was analyzed by an ion chromatograph (ICS-900, Dionex Corporation).

3. Results and discussion

Determination of a suitable solution is the first step to fabricate nanostructured Cu–Au alloys on NCF/Cu. Fig. 1a shows the reduction behavior of Cu^{2+} and $AuCl_4^-$ on the surface of Cu electrode. In a solution of 5 mM $CuSO_4$, the strong reduction peak at −0.68 V is associated with bulk deposition of Cu (0) (black line) while the weak peak at −0.22 V results from the reduction of Cu(II) to Cu(I). As for the solution containing 5 mM $HAuCl_4$, the cathodic peak at −0.03 V is ascribed to the deposition of Au(0) (red line). When both $CuSO_4$ and $HAuCl_4$ are present in solution, the characteristic peak corresponding to the deposition of Cu disappears and a new cathodic peak appears at −0.16 V (blue line), which is probably attributed to the co-reduction of Cu^{2+} and $AuCl_4^-$ into Cu–Au alloy (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.).

A similar electrochemical technique was used to deposit Cu–Au onto NCF electrode at −0.26 V and XPS analysis indicates its composition to be $Cu_{63.9}Au_{36.1}$. XRD results for this Cu–Au deposit plus a pure Au deposit (from 5 mM $HAuCl_4$ at the same potential) are shown in Fig. 1b. The diffraction peaks of Cu resulted from that of porous copper film. As for pure Au deposited on NCF, diffraction peaks at 38.2, 44.5, 64.8 and 77.6° can be ascribed to Au (111), (200), (220) and (311) reflections, respectively. Different from that of pure

Au, the diffraction peaks of Cu–Au samples shift to higher diffraction angles, indicating that the deposit is composed of Cu–Au alloy. Fig. 1c and d shows SEM images depicting the morphology of the original NCF and that after deposition of the Cu–Au film, respectively. The original NCF is a kind of 3D nanostructured network with ligaments of approximately 40 nm in size (Fig. 1c). After deposition of Cu–Au alloy, the ligament size of NCF increases to ∼70 nm but the 3D nanostructured networks remain (Fig. 1d), indicating that Cu–Au is mostly deposited on the surface of ligaments. It can be seen that the surface of ligaments is not smooth and there are very fine nanoparticles (less than ∼20 nm) on the surface. However, Cu–Au nanoparticles deposited on a smooth copper substrate are much bigger (∼70 nm, Fig. 1e), indicating that the porous structure of NCF has a great effect on the morphology of deposited Cu-Au nanoparticles.

Electrochemical reduction of CO_2 was investigated on different Cu electrodes and results are shown in Fig. 2. Using $Cu_{63.9}Au_{36.1}$/NCF electrode, hydrogen evolution occurs at about −1.1 V in the Ar bubbled solution (Fig. 2a). In presence of CO_2, the cathodic current increases at potential more negative than −1.0 V, indicating that participation of CO_2 reduction contributes to the enhancement of cathodic current. In comparison, hydrogen evolution starts at −1.0 V and the current is slightly suppressed by CO_2 reduction on nanostructured Cu electrode (Fig. 2b). Such suppression occurs owing to presence of adsorbed species generated during CO_2 reduction [12]. The difference in electrochemical behaviors indicates that the nanostructured Cu–Au alloy may favor conversion of CO_2 and its intermediate species, which leads to the increase of current in presence of CO_2. However, only current−potential relationships are not enough to judge if these materials could catalyze conversion of CO_2 into alcohols. It is necessary to quantitatively analyze the products after bulk electrolysis of CO_2.

The presence of alcohols in liquid products is confirmed through GC analysis, and the peaks correspond to methanol (2.21 min) and ethanol (2.66 min), respectively (Fig. 2c). With pure Cu plate as
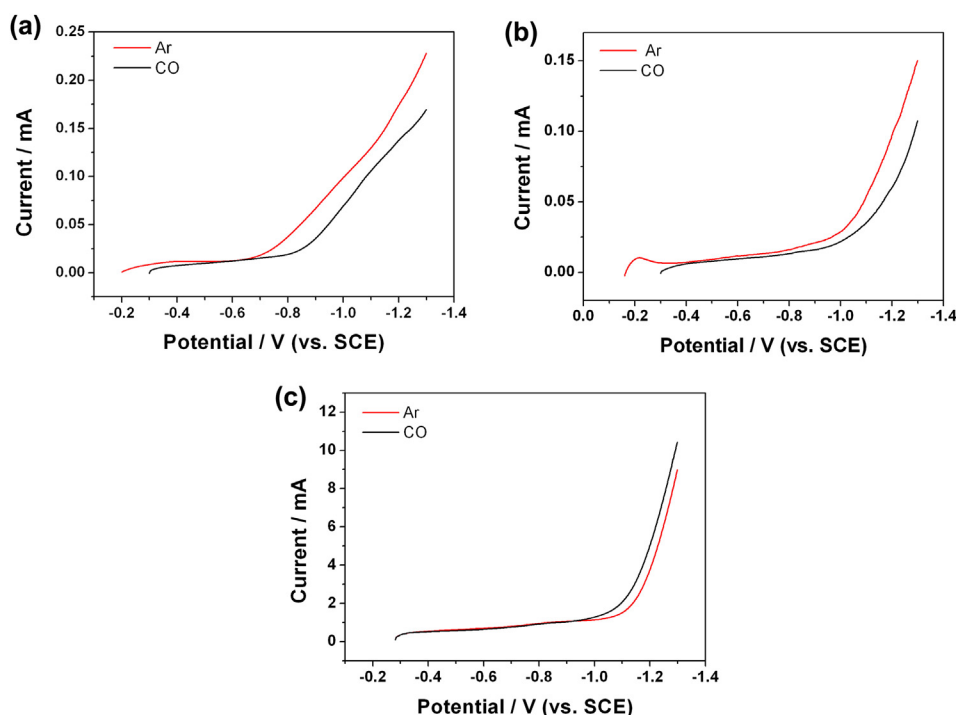

Fig. 3. LSV curves of nanostructured Au (a), nanostructured Cu (b), and $Cu_{63.9}Au_{36.1}$/NCF (c) in 0.2 M PBS solution saturated with Ar (red line) and CO (black line) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

electrode, the faradic efficiencies of methanol and ethanol are 0.8% and 4%, respectively (Fig. 2d). In sharp contrast, the faradic efficiency of methanol on $Cu_{63.9}Au_{36.1}$ electrode is 15.9%, almost 19 times that for pure Cu. In addition, the faradic efficiency of ethanol is increased to 12%. Pure Cu nanoparticles of similar size were also tested for CO_2 reduction, and the corresponding faradic efficiencies of methanol (5.1%) and ethanol (4.6%) are higher than that on bulk Cu but still much lower than that on $Cu_{63.9}Au_{36.1}$/NCF. Similar pure gold nanoparticles were found not to produce alcohols. These results suggest that Au component in nanostructured Cu–Au alloy may contribute a lot to enhanced conversion of CO_2 to alcohols. To investigate if the nanostructure also affected the catalysis performance, we tested Cu–Au alloy deposited on smooth copper as working electrode (Fig. 1e) for CO_2 reduction. The as-synthesized Cu–Au alloy is analyzed to be $Cu_{62.6}Au_{37.4}$, close to that deposited on NCF. However, the faradic efficiencies of methanol and ethanol are only 7.9% and 3.5%, which are much lower than that of $Cu_{63.9}Au_{36.1}$/NCF. This result indicates that the size and nanostructure of Cu–Au also affect the conversion efficiencies of alcohols.

Besides alcohols, formate is another major product of CO_2 reduction and analysis results are listed in Table 1. The faradic efficiency of formate on nanostructured Cu was much higher than that on $Cu_{63.9}Au_{36.1}$/NCF. To investigate the effect of Cu content on faradic efficiencies of products from CO_2 conversion, different Cu–Au/NCF samples with similar nanostructure were prepared by adjustment of deposition potential. With a higher atomic percentage of Cu in Cu–Au alloys, the faradic efficiency of formate increased while that of alcohols decreased. The results in Table 1 indicate that the suitable addition of Au into Cu alloys may facilitate the reduction of CO_2 to alcohols while restraining the formation of formate. According to the publications, two-electron reduction of CO_2 to formate or CO was more favorable due to low overpotential [13]. As for the formate, it is identified to be a stable end product and much harder to be reduced into other products (e.g. alcohols) [14,15]. Alternatively, CO is believed to be an important intermediate species, which could be further converted to hydrocarbons or methanol [15]. However, the yield of methanol on pure copper electrode is known much lower than that of CO over a wide potential range [16]. If CO reduction was facilitated, there could be a possibility for the enhancement of further conversion to methanol.

To investigate if as-prepared $Cu_{63.9}Au_{36.1}$/NCF could catalyze conversion of intermediate product – CO, electrochemical behaviors of nanostructured Cu, nanostructured Au and $Cu_{63.9}Au_{36.1}$/NCF electrodes were tested in solutions saturated with either Ar or CO. Note that the pH values of both the CO-saturated and Ar-saturated solutions were measured to be close, eliminating effects of proton concentrations on the hydrogen evolution. Fig. 3a shows that hydrogen evolution current is obviously suppressed on nanostructured Cu electrode when CO is present owing to the adsorption of CO on the surface [16]. Similar results are also obtained on the nanostructured Au electrode (Fig. 3b). With $Cu_{63.9}Au_{36.1}$/NCF as electrode, cathodic current is improved in presence of CO at

potentials less than −0.9 V (Fig. 3c), indicating reduction of CO occurs on $Cu_{63.9}Au_{36.1}$/NCF. Hence it does appear likely that the alloys facilitate enhanced alcohol production through catalyzing conversion of intermediary CO. Although underlying catalytic mechanism of Cu–Au alloys is not clear, we expect that results presented here can provide new solution for electrochemical conversion of CO_2.

4. Conclusions

Nanostructured Cu–Au alloys were developed by a template-assisted electrodeposition and showed special catalytic activity towards electrochemical reduction of CO_2 to alcohols (methanol or ethanol) in aqueous system. Faradic efficiency of methanol on $Cu_{63.9}Au_{36.1}$/NCF was analyzed to be 15.9%, which was about 19 times that on pure Cu. In addition, faradic efficiency of ethanol was improved to 12%. Electrochemical analysis showed that Cu–Au alloys catalyzed not only CO_2 reduction, but also CO reduction. The surprisingly multifunctional catalysis of Cu–Au alloys contributed greatly to the enhanced conversion of CO_2 to alcohols. This kind of nanostructured Cu–Au alloys was believed to be promising catalysts in conversion of CO_2 to alcohols.

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